**DIBUTYLTIN(IV)
ALKYLCYCLOHEXYLDITHIOCARBAMATES:
SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL
STRUCTURES OF DIBUTYLTIN(IV) N-METHYL AND
N-ETHYLCYCLOHEXYLDITHIOCARBAMATE**

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ABSTRACT

A new series of dibutyltin(IV) alkylcyclohexyldithiocarbamates of the type $(C_4H_9)_2Sn[S_2CNR(C_6H_{11})]_2$ ($R = CH_3, C_2H_5, i-C_3H_7$) have been successfully synthesized using *in-situ* method. These compounds were characterized by elemental analysis, infrared and ^{13}C NMR spectroscopy. A single crystal X-ray analysis of dibutyltin(IV) ethylcyclohexyldithiocarbamate, $(C_4H_9)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$ (compound **2**) showed that the system of this crystal is triclinic with space group *P*-1 while dibutyltin(IV) methylcyclohexyldithiocarbamate, $(C_4H_9)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$ (compound **1**) has monoclinic system and its space group is *P*2₁/c. In the crystal structure of compound **2**, the dithiocarbamate ligands are bidentically chelated to the tin atom with non-equivalent of the Sn-S distances: Sn(1)-S(1) = 2.9255(11) and Sn(1)-S(2) = 2.5419(10); Sn(1)-S(3) = 2.8922(9) and Sn(1)-S(4) = 2.5293(10) Å while in compound **1**, the dithiocarbamate ligands were anisobidentically chelated to the tin atom.

Keywords: dibutyltin(IV); dithiocarbamate; crystal structure

1. INTRODUCTION

The rapid rise in the industrial, agricultural and biological applications of organotin(IV) compounds during the last few decades has led to their accumulation in the environment and in biological systems. In recent years much attention have been paid to the synthesis, characterization and biological activities of various organotin(IV) derivatives with sulfur ligands like thione or dithiocarbamate [1 - 3]. Organotin(IV) dithiocarbamate compounds have been the subject of numerous spectroscopic and structural studies of their industrial importance and their

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antifungal and insecticidal properties. The increase in study of these compounds also because of their varied structures. The crystallographic studies of the dithiocarbamate compounds of diorganotin(IV) showed that the coordination environments around the central atom ranging from tetrahedral to distorted octahedral with the dithiocarbamate groups can act as either unidentate or bidentate ligand [4]. In our previous publications, we have reported that in $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{11})]_2$, both of the dithiocarbamate groups act as isobidentate ligand [5] and similar observation was also made for $\text{Me}_2\text{Sn}[\text{S}_2\text{CNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2]_2$ [6]. In this paper, we report the synthesis of three new dibutyltin(IV) dithiocarbamates and their spectroscopic characterization. The crystal structure two of these compounds also will be discussed in this paper.

2. EXPERIMENTAL

2.1 Materials

All chemicals and solvents were of analytical grade, *N*-methylcyclohexylamine, *N*-ethylcyclohexylamine, *N*-isopropylcyclohexylamine and dibutyltin(IV) chloride were purchased from Fluka while chloroform and ethanol were supplied by Merck. All the chemicals were used as received.

2.2 Preparation of compounds

Three dibutyltin(IV) alkylcyclohexyldithiocarbamate compounds - $(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{11})]_2$ (compound **1**), $(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_{11})]_2$ (compound **2**) and $(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(i\text{C}_3\text{H}_7)(\text{C}_6\text{H}_{11})]_2$ (compound **3**) were prepared using direct reaction by addition of carbon disulphide, CS_2 (30×10^{-3} mol) to an ethanolic solution of corresponding secondary amine (30×10^{-3} mol). The mixture was stirred for one hour at 0 - 4°C. After one hour of stirring, the dibutyltin(IV) chloride solution was added and stirred for another one hour. The white precipitate was filtered and washed with cold ethanol and dried in vacuo over silica gel. The yield and melting point were recorded for each compound. Recrystallization from a CHCl_3 :ethanol = 1:1 (v:v) mixture yielded colourless crystal of compound **1** and **2**.

2.3 Instrumentations

Melting points were determined on an Electrothermal IA 9100 instrument. The analyses for carbon, hydrogen, nitrogen and sulfur were carried out using a Fison EA 1108. The percentage of tin element in the compounds was determined gravimetrically by igniting a known quantity of each compound to SnO_2 . The IR spectra were recorded using a Perkin Elmer GX spectrophotometer; KBr disc for the range 400 - 4000 cm^{-1} and nujol in polyethylene tablets for the range 400 - 250 cm^{-1} . ^{13}C NMR spectra was recorded in CDCl_3 on a Joel JNM-LA 400 using TMS as internal standard. Bruker SMART CCD was used to record X-ray single structure determination. All these measurements were done at School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia.

2.4 Crystallographic Studies

Suitable crystals for X-Ray analysis of compounds **1** and **2** were formed after the mixture of chloroform and ethanol solutions were allowed to slowly evaporate for a few days. Data collection: SMART [7]. Cell refinement: SAINT [7]. Data reduction: SAINT. Programs were used to solve structure: *SHELXTL* [8]. Molecular graphics: *SHELXTL* [8].

3. RESULTS AND DISCUSSION

The direct reaction of Bu_2SnCl_2 with the corresponding amines and carbon disulphide in 1:2:2 molar ratio yields the dibutyltin(IV) dithiocarbamates in a good percentage. The physical and analytical data for compounds **1** to **3** are given in Table 1. Elemental analytical data obtained are in agreement with the proposed molecular formulae. All of these compounds are soluble in chloroform, CHCl_3 and stable in air. A general reaction scheme for the above preparation is given in Figure 1.

Fig.1: The reactions between *N*-alkyl-*N*-cyclohexylamine, carbon disulfide and dibutyltin(IV) chloride.

Table 1: Physical and elemental analysis data of dibutyltin(IV) *N*-alkyl-*N*-cyclohexyldithiocarbamate compounds.

Molecular formula	Colour	Yield (%)	Melting point (°C)	Found(Calculated) (%)				
				C	H	N	S	Sn
$(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{11})]_2$ (compound 1)	White	83	122.6 - 124.0	47.15 47.29	8.08 7.55	4.62 4.60	22.72 21.02	17.92 19.54
$(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{11})]_2$ (compound 2)	White	79	110.6 - 112.0	49.00 48.98	8.38 7.85	4.11 4.40	20.23 20.09	20.21 18.65
$(\text{C}_4\text{H}_9)_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{11})]_2$ (compound 3)	White	76	137.7 - 148.8	49.92 50.53	9.19 8.12	4.16 4.21	18.08 19.25	19.48 17.89

The important peaks in the infrared spectra of the compounds are showned in Table 2. The appearance of a strong band in the $1475 - 1479 \text{ cm}^{-1}$ region, attributed to a $\text{S}_2 \text{---} \text{CN}$ stretching mode [9] that we called “thioureida band”. This band is very sensitive to the substituents on the tin atom, moving to a higher frequency by the introduction of more electronegative substituents. While the band present in the $978 - 998 \text{ cm}^{-1}$ region attributed to $\nu(\text{C} \text{---} \text{S})$ vibration which the behaviour of the dithiocarbamate ligands in these compounds may be predicted on the basis of this band stretching mode. The presence of only one sharp band at $985 \pm 15 \text{ cm}^{-1}$ indicates the bidentate nature of the dithiocarbamate ligand in the compounds [10]. The presence of another one band in the $375 - 389 \text{ cm}^{-1}$ region was attributed to $\nu(\text{Sn-S})$, confirming the bonding of the central tin atom with the sulfur atom of the dithiocarbamate ligand.

Table 2: The important infrared absorption bands (cm^{-1}).

Compound	$\nu(\text{C} \text{---} \text{N})$	$\nu(\text{C} \text{---} \text{S})$	$\nu(\text{Sn-S})$
1	1478 s	979 m	375 m
2	1475 s	998 m	385 s
3	1479 s	978 w	389 s

s = strong, m = medium, w = weak.

Table 3: ^{13}C NMR spectra data of compound **1-3** (δ , ppm).

Compound	N ¹³ CS ₂	R(C ₆ H ₁₁)	Sn-Bu	N-R'(R' = CH ₃ , C ₂ H ₅ , <i>i</i> -C ₃ H ₇)
1	199.82	63.50	34.57	36.03
		30.14	28.78	
		25.69	26.69	
		25.57	14.06	
2	199.34	63.74	34.37	43.86
		30.69	28.56	14.13
		25.60	26.44	
		25.32	13.87	
3	199.44	66.50	34.56	54.74
		29.59	28.73	19.64
		26.63	28.11	
		26.47	14.15	

Table 4: Crystallographic data and refinement parameters for compound **1** and **2**.

	Compound 1	Compound 2
Empirical Formula	C ₂₄ H ₄₆ N ₂ S ₄ Sn	C ₂₆ H ₅₀ N ₂ S ₄ Sn
Formula weight	609.56	637.71
Crystal system	Monoclinic	Trilinic
Space group	P2(1)/c	P-1
Crystal size(mm)	0.53 × 0.42 × 0.38	0.35 × 0.25 × 0.25
<i>a</i> (Å)	10.478(2)	10.2809(6)
<i>b</i> (Å)	11.584(2)	11.435(3)
<i>c</i> (Å)	24.783(4)	11.989(3)
α (°)	90	103.1030(10)
β (°)	99.897(5)	108.1250(10)
γ (°)	90	90.6550(10)
<i>V</i> (Å ³)	2949.6(3)	1591.49(15)
<i>Z</i>	5	2
<i>D</i> /Mgm ⁻³	1.366	1.324
μ (mm ⁻¹)	1.158	1.081
<i>F</i> (000)	1272	662
Colour	Colourless	Colourless
Temperature (<i>K</i>)	293(2)	293(2)
θ range (°)	1.97 - 23.24	1.65 - 27.53
Index ranges ($\pm h, \pm k, \pm l$)	-11/4, -12/6, -22/21	-13/13, -16/16, -17/17
Reflection collected/unique	4598/3276	20785/7307
	[<i>R</i> _{int} = 0.0635]	[<i>R</i> _{int} = 0.0237]
Final <i>R</i> indices <i>I</i> > 2σ(<i>I</i>)	<i>R</i> ₁ = 0.0509, w <i>R</i> ₂ = 0.0695	<i>R</i> ₁ = 0.0470, w <i>R</i> ₂ = 0.1216
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0585, w <i>R</i> ₂ = 0.1448	<i>R</i> ₁ = 0.0546, w <i>R</i> ₂ = 0.1279
Largest diff. peak and hole (e Å ⁻³)	1.162 and -0.559	1.609 and -0.481

The ^{13}C NMR spectra of these compounds was carried out in CDCl_3 , and showed that the peak for N^{13}CS_2 chemical shifts appeared at 199.34 - 199.82 ppm region (Table 3). The signals for the butyl carbons attached to the tin atom have been observed in the range which agree with the compound reported by [11](13.74 - 34.19 ppm).

Suitable crystals for X-ray analysis of compounds **1** and **2** were obtained by slow evaporation of a chloroform:ethanol mixture at room temperature for a few days. X-ray data collections carried out at room temperature. The details of the crystal data and refinement parameters for compound **1** and **2** are listed in Table 4 while the selected geometric parameters are listed in Table 5 and 6 respectively. The structure were solved by direct methods using SHELXS-97 and refined by full-matrix least-square calculations, using the program system SHELXS-97.

Table 5: Selected geometric parameter ($\text{\AA}$, $^\circ$) for compound **1**.

Bond length ($\text{\AA}$)			
Sn(1)–S(4)	2.494(2)	S(3)–C(17)	1.686(8)
Sn(1)–S(2)	2.528(2)	S(4)–C(17)	1.744(8)
Sn(1)–C(13)	2.111(7)	N(1)–C(8)	1.328(9)
Sn(1)–C(9)	2.165(8)	N(2)–C(19)	1.484(9)
S(1)–C(8)	1.691(8)	S(2)–C(8)	1.758(7)
Bond angle ($^\circ$)			
C(13)–Sn(1)–C(9)	129.7(4)	C(9)–Sn(1)–S(2)	109.1(3)
C(13)–Sn(1)–S(4)	109.28(19)	S(4)–Sn(1)–S(2)	82.25(7)
C(9)–Sn(1)–S(4)	111.2(3)	C(8)–S(2)–Sn(1)	95.0(3)
C(13)–Sn(1)–S(2)	104.8(2)	C(17)–S(4)–Sn(1)	95.8(2)

Fig. 2: ORTEP plot of compound **1** at the 50% probability level.

Figure 2 and 3 showed ORTEP plot of the molecules in the unit cell which showed that tin atom in compound **1** and **2** was chelated by both of sulphur atoms of the dithiocarbamate group which formed six-coordinated compound. The selected geometric parameters for these compound were summarized in Table 5 and 6. The geometry of the tin central atom in compound **1** is expanded from severely distorted tetrahedral to a distorted octahedral due to the weak intramolecular Sn(1)···S(1) and Sn(1)···S(3) interactions with the Bu-Sn-Bu angle of 129.7(4) Å is in non-linear axial positions. This value is slightly smaller with the reported value of Me-Sn-Me angle in Me₂Sn[S₂CN(CH₃)(C₆H₁₁)]₂ of 137.0(2) Å [5]. While in compound **2**, the dithiocarbamate ligands are bidentately chelated to the tin atom with one longer [Sn(1)-S(1) = 2.9255(11) Å; Sn(1)-S(3) = 2.8922(9) Å] and one shorter [(Sn(1)-S(2) = 2.5419(10); Sn(1)-S(4) = 2.5293(10) Å) Sn-S bond respectively. These values are closed to those observed earlier in Me₂Sn[S₂CN(CH₂CH₂CH₂CH₂CH₂)]₂ [6]. The long Sn-S distances are significantly less than the sum of the van der Waal's radii (4.0) [6].

Table 6: Selected geometric parameter (Å, °) for compound **2**.

Bond length (Å)			
Sn(1)–S(1)	2.9255(11)	S(1)–C(9)	1.692(4)
Sn(1)–S(2)	2.5419(10)	S(2)–C(9)	1.746(3)
Sn(1)–S(3)	2.8922(9)	S(3)–C(18)	1.692(4)
Sn(1)–S(4)	2.5293(10)	S(4)–C(18)	1.743(4)
Sn(1)–C(10)	2.128(4)	C(9)–N(1)	1.328(4)
Sn(1)–C(14)	2.144(5)	C(18)–N(2)	1.331(4)
Bond angle (°)			
S(4)–Sn(1)–S(2)	85.36(3)	C(14)–Sn(1)–S(4)	103.11(17)
S(3)–Sn(1)–S(1)	144.12(3)	C(18)–S(4)–Sn(1)	93.30(12)
C(10)–Sn(1)–C(14)	144.7(2)	C(18)–S(3)–Sn(1)	82.46(11)
C(10)–Sn(1)–S(4)	102.17(12)	S(3)–C(18)–S(4)	118.60(19)

Fig. 3: ORTEP plot of compound **2** at the 50% probability level.

4. CONCLUSION

The elemental, spectroscopic and supported by crystallographic data approved that dithiocarbamate anions have chelated to the tin atom to form the neutral compounds. The crystallographic information obtained for dibutyltin(IV) methyl and ethyldithiocarbamate showed that the dithiocarbamate ligands formed an isobidentate and bidentate chelation respectively with non-equivalent Sn-S bond distances. This concluded that the substituent groups of the dithiocarbamate ligands have an influence on the chelation of the dithiocarbamate ligands to the tin atom.

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